

## Patent Abstracts of Japan

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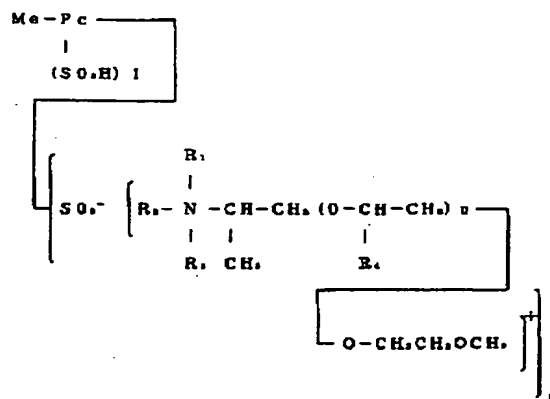
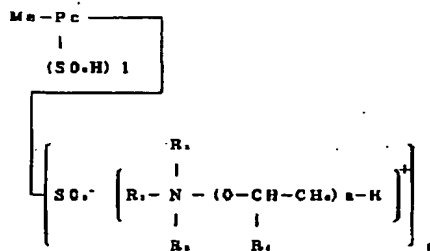
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APPLICATION NUMBER : 10136647

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INT.CL. : C09B 67/20 C09D 11/02

TITLE : PIGMENT COMPOSITION AND INK  
CONTAINING SAME



ABSTRACT : PROBLEM TO BE SOLVED: To obtain a pigment composition having excellent flowability and gloss by mixing a metal phthalocyanine and/or a halogenated metal phthalocyanine with a metal phthalocyaninesulfonic acid polyoxyalkyleneammonium and/or a halogenated metal phthalocyaninesulfonic acid polyoxyammonium.

SOLUTION: There is provided a pigment composition comprising 100 pts.wt. metal phthalocyanine and/or halogenated metal phthalocyanine and 1-30 pts.wt. metal phthalocyaninesulfonic acid polyoxyalkyleneammonium and/or halogenated metal phthalocyaninesulfonic acid polyoxyalkyleneammonium represented by formula I or II. This composition is mixed with a liquid synthetic resin vehicle and a solvent to prepare a gravure ink. In the formulae, Me is a di- or tri-valent metal atom; Pc is a phthalocyanine ring; R<sub>1</sub> to R<sub>3</sub> are each H or a 1-5C alkyl; R<sub>4</sub> is H or methyl; n is 2-100; and I+m=1-4.

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L85 ANSWER 14 OF 75 HCA COPYRIGHT 2002 ACS  
 AN 131:352651 HCA  
 TI Pigment compositions and inks therefrom  
 IN Yamaguchi, Akira; Takahashi, Masayoshi  
 PA Dainippon Ink and Chemicals, Inc., Japan  
 SO Jpn. Kokai Tokkyo Koho, 8 pp.  
 CODEN: JKXXAF

DT Patent  
 LA Japanese  
 IC ICM C09B067-20  
 ICS C09B067-20; C09D011-02  
 CC 42-10 (Coatings, Inks, and Related Products)  
 Section cross-reference(s): 41

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 11323166	A2	19991126	JP 1998-136647	19980519
AB	Pigments contain (un)halogenated metal phthalocyanines and (un)halogenated metal phthalocyanine sulfonic acid polyoxyalkylene ammonium salts. Thus, a nitrocellulosic gravure ink contained Cu phthalocyanine and a salt of Cu phthalocyanine sulfonic acid with Adekacol CC 36.				
ST	gravure ink pigment copper phthalocyanine; polyoxyalkylene ammonium phthalocyanine sulfonic acid salt				
IT	Inks (gravure; pigment compns. contg. (un)halogenated metal phthalocyanines and (un)halogenated metal phthalocyanine sulfonic acid polyoxyalkylene ammonium salts for inks)				
IT	Pigments, nonbiological (pigment compns. contg. (un)halogenated metal phthalocyanines and (un)halogenated metal phthalocyanine sulfonic acid polyoxyalkylene ammonium salts for inks)				
IT	Quaternary ammonium compounds, uses RL: TEM (Technical or engineered material use); USES (Uses) (polyoxyalkylene; pigment compns. contg. (un)halogenated metal phthalocyanines and (un)halogenated metal phthalocyanine sulfonic acid polyoxyalkylene ammonium salts for inks)				
IT	83713-01-3D, Jeffamine M 2005, salts with copper phthalocyanine sulfonic acid RL: TEM (Technical or engineered material use); USES (Uses) (Jeffamine M 2005; pigment compns. contg. (un)halogenated metal phthalocyanines and (un)halogenated metal phthalocyanine sulfonic acid polyoxyalkylene ammonium salts for inks)				
IT	9042-76-6P 28901-96-4DP, Copper phthalocyanine monosulfonic acid, polyoxyalkylene ammonium salts RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses) (pigment compns. contg. (un)halogenated metal phthalocyanines and (un)halogenated metal phthalocyanine sulfonic acid polyoxyalkylene ammonium salts for inks)				
IT	147-14-8, Copper phthalocyanine RL: TEM (Technical or engineered material use); USES (Uses) (pigment compns. contg. (un)halogenated metal phthalocyanines and (un)halogenated metal phthalocyanine sulfonic acid polyoxyalkylene ammonium salts for inks)				

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			L
C09D 11/02		C09D 11/02	

Request for Examination Not Received

Number of Claims 7 OL (Total 8 sheets)

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**(54) [Title of the Invention]**

A pigment composition and an ink containing same

**(57) [Abstract]**

[Problem] To provide a pigment composition which enables a viscosity reduction in the form of a gravure ink to be realized and, furthermore, where the gloss of the colour applied using this ink is outstanding.

[Resolution Means] A pigment composition comprising a metal phthalocyanine and/or a halogenated metal phthalocyanine, plus a metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt and/or a halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt. A gravure ink containing said pigment composition.

**[Scope of Claims]**

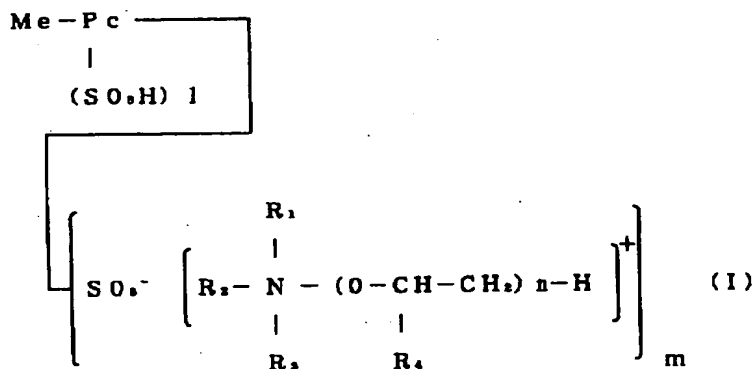
**[Claim 1]** A pigment composition which is characterized in that, in a pigment composition containing a metal phthalocyanine and/or a halogenated metal phthalocyanine (A) and a metal phthalocyaninesulphonic acid ammonium salt (B), there is used, as this metal phthalocyaninesulphonic acid ammonium salt (B), a metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt and/or a halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt.

**[Claim 2]** A composition according to Claim 1 where the metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt is a metal phthalocyaninesulphonic acid polyoxypropyleneammonium salt or a halogenated metal

phthalocyaninesulphonic acid polyoxypropyleneammonium salt.

**[Claim 3]** A composition according to Claim 1 where the metal phthalocyaninesulphonic acid polyoxyalkylene-ammonium salt is represented by formula (I).

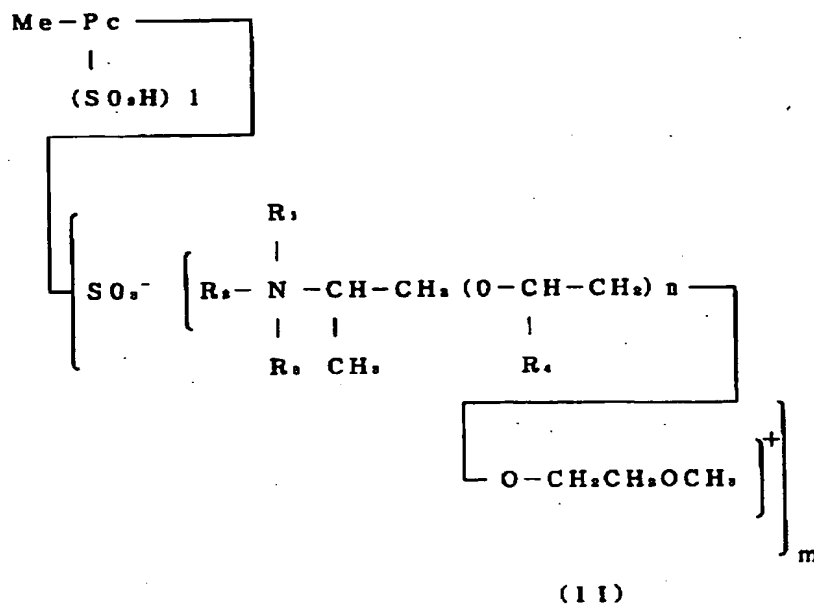
[Chem.1]



In general formula (I), Me represents a divalent or trivalent metal atom, and Pc represents a phthalocyanine ring where hydrogen atoms on the ring may be replaced by halogen atoms. R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are identical or different and represent hydrogen atoms or C<sub>1-5</sub> alkyl groups. R<sub>4</sub> represents a hydrogen atom or a methyl group. n is 2 to 100, and (1 + m) = 1 to 4.

**[Claim 4]** A composition according to Claim 1 where the metal phthalocyaninesulphonic acid polyoxyalkylene-ammonium salt is represented by formula (II).

[Chem.2]



In general formula (II), Me represents a divalent or trivalent metal atom, and Pc represents a phthalocyanine ring where hydrogen atoms on the ring may be replaced by halogen atoms. R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are identical or different and represent hydrogen atoms or C<sub>1-5</sub> alkyl groups. R<sub>4</sub> represents a hydrogen atom or a methyl group. n is 1 to 100, and (1 + m) = 1 to 4.

**[Claim 5]** A composition according to Claim 1 where the metal phthalocyaninesulphonic acid polyoxyalkylene-ammonium salt only has one metal phthalocyanine residue.

**[Claim 6]** A composition according to Claim 1 which contains 1 to 30 parts by weight of the metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt and/or halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt (B) per 100 parts by weight of the metal phthalocyanine and/or halogenated metal phthalocyanine (A).

**[Claim 7]** A gravure ink where a composition according to Claim 1 is dispersed as the colouring agent in a liquid synthetic resin vehicle (C).

**[Detailed Description of the Invention]**

[0001]

[Technical Field of the Invention] The present invention relates to a pigment composition and to an ink containing same.

[0002]

[Prior-Art] Known pigment compositions encompass an extremely diverse range of materials. For example, in JP-A-57-12067, there is described a pigment composition containing a metal phthalocyanine and/or a halogenated metal phthalocyanine plus a metal phthalocyanine-sulphonic acid ammonium salt, where there is used, as said metal phthalocyaninesulphonic acid ammonium salt, a salt formed between an unhalogenated "metal phthalocyaninesulphonic acid and a tertiary amine having alkyl groups".

[0003] Moreover, from JP-A-3-33166, there is already known a pigment composition containing halogenated copper phthalocyanine and halogenated copper phthalocyaninesulphonic acid ammonium salt where there is used, as said halogenated copper phthalocyanine-sulphonic acid ammonium salt, the "salt of halogenated copper phthalocyaninesulphonic acid and a tertiary amine having alkyl groups".

[0004]

[Problem to be Resolved by the Invention] However, in all the aforesaid disclosed pigment compositions the tertiary amines forming the sulphonic acid ammonium salt substantially comprise only alkyl groups and so, in terms of the fluidity of pigment compositions containing such a sulphonic acid salt, the viscosity is high and flow properties inadequate. Moreover, gravure inks prepared by mixing such pigment compositions with an ink vehicle show inadequate gloss.

[0005]

[Means for Resolving the Problem] The present inventors have carried out a painstaking investigation in view of this situation and, as a result, have discovered that by incorporating, as the metal phthalocyaninesulphonic acid ammonium salt, one which contains oxyalkylene bonds in the structure of the ammonium salt moiety, all the aforesaid problems are resolved. The present invention has been perfected based on this discovery.

[0006] Specifically, the present invention encompasses the following:-

[0007] 1. A pigment composition which is characterized in that, in a pigment composition containing a metal phthalocyanine and/or a halogenated metal phthalocyanine (A) and a metal phthalocyaninesulphonic acid ammonium salt (B), there is used as said metal phthalocyaninesulphonic acid ammonium salt (B) a metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt and/or a halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt.

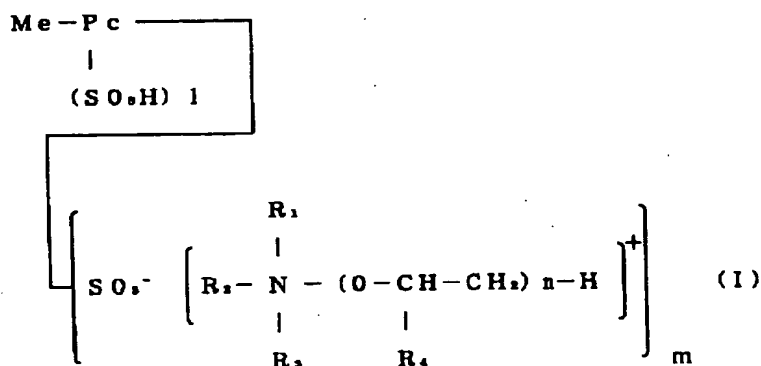


[0008] 2. A composition according to 1 where the metal phthalocyaninesulphonic acid polyoxyalkylene-ammonium salt is a metal phthalocyaninesulphonic acid polyoxypropyleneammonium salt or a halogenated metal phthalocyaninesulphonic acid polyoxypropyleneammonium salt.

[0009] 3. A composition according to 1 where the metal phthalocyaninesulphonic acid polyoxyalkylene-ammonium salt is represented by formula (I).

[0010]

[Chem.3]

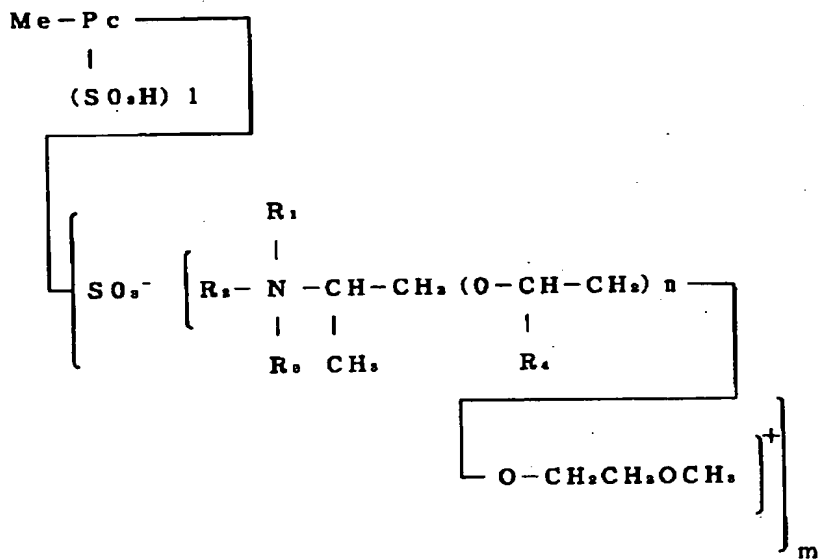


[0011] In general formula (I), Me represents a divalent or trivalent metal atom, and Pc represents a phthalocyanine ring where hydrogen atoms on the ring may be replaced by halogen atoms. R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are identical or different and represent hydrogen atoms or C<sub>1-5</sub> alkyl groups. R<sub>4</sub> represents a hydrogen atom or a methyl group. n is 2 to 100, and (1 + m) = 1 to 4.

[0012] 4. A composition according to 1 where the metal phthalocyaninesulphonic acid polyoxyalkylene-ammonium salt is represented by formula (II).

[0013]

[Chem. 4]



(II)

[0014] In general formula (II), Me represents a divalent or trivalent metal atom, and Pc represents a phthalocyanine ring where hydrogen atoms on the ring may be replaced by halogen atoms. R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are identical or different and represent hydrogen atoms or C<sub>1-5</sub> alkyl groups. R<sub>4</sub> represents a hydrogen atom or a methyl group. n is 1 to 100, and (1 + m) = 1 to 4.

[0015] 5. A composition according to 1, 2, 3 or 4 above where the metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt only has one metal phthalocyanine residue.

[0016] 6. A composition according to 1, 2, 3, 4 or 5 above which contains 1 to 30 parts by weight of the metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt and/or halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt (B) per 100

parts by weight of the metal phthalocyanine and/or halogenated metal phthalocyanine (A).

[0017] A gravure ink where a composition according to 1, 2, 3, 4, 5 or 6 above is dispersed as colouring agent in a liquid synthetic resin vehicle (C).

[0018] Component (A) employed in the present invention is an optionally-halogenated metal phthalocyanine (A). For this purpose, there may be employed any generally known such material which is either a metal phthalocyanine or a halogenated metal phthalocyanine. In the present invention, metal phthalocyanine refers to a metal phthalocyanine which has not been halogenated.

[0019] Specific examples of component (A) are metal phthalocyanines containing, for example, copper, nickel, cobalt, titanium or aluminium in the phthalocyanine ring, and halogenated metal phthalocyanines comprising these same metal phthalocyanines containing halogen atoms such as chlorine atoms or bromine atoms. There are no particular restrictions on the proportion of halogen atoms contained in the halogenated metal phthalocyanines, and low-chlorinated, low-brominated, high-chlorinated, high-brominated and mixed halogenated metal phthalocyanines, etc, may all be used.

[0020] These metal phthalocyanines and halogenated metal phthalocyanines may respectively be used on their own, or two or more different types may be employed in combination.

[0021] Component (A) can also optionally be employed after a surface treatment, such as a rosin treatment or

a surfactant treatment. Moreover, component (A) can also be used in any form such as that of a slurry, wet cake, dry powder or the like.

[0022] The metal phthalocyaninesulphonic acid ammonium salt (B) used in the present invention is an unhalogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt and/or a halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt. These are characterized in that they include a skeletal structure based on repeating oxyalkylene bonds in the molecule.

[0023] Examples of these oxyalkylene bonds are oxyethylene, oxypropylene, oxytetramethylene and oxytetramethylene with a lower alkyl group on a carbon atom, or a structure comprising two or more types of these in the form of a block copolymer or random copolymer. The oxyalkylene terminal may be a hydroxyl group, or it may be blocked with an alkoxy group such as a methoxy group.

[0024] The unhalogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt and/or halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt can be used on its own or two or more types thereof may be jointly employed.

[0025] As the unhalogenated metal phthalocyanine-sulphonic acid polyoxyalkyleneammonium salt and/or halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt, a substance having only one phthalocyanine-ring-based phthalocyanine residual

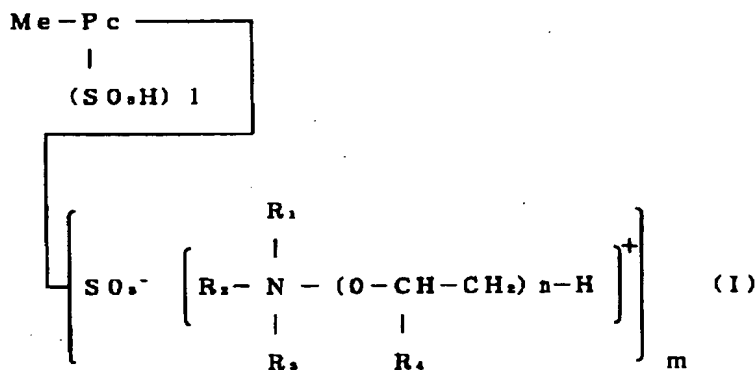
group in the molecule is preferred in terms of still better fluidity.

[0026] An unhalogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt is preferred compared to a halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt, in that its bleed resistance is more outstanding.

[0027] As a general formula for the optionally-halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salts favourably used in the present invention, the metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salts represented by the following general formula (I) are preferred.

[0028]

[Chem.5]



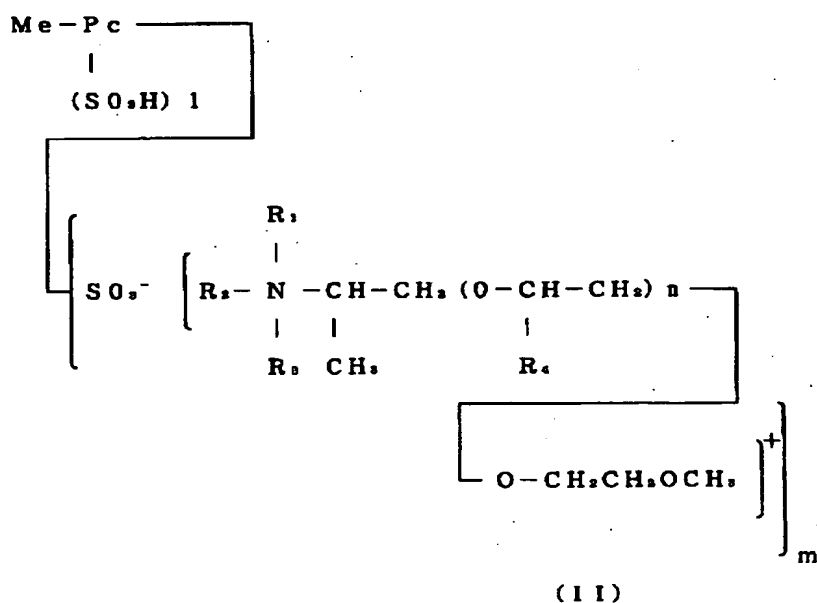
[0029] In general formula (I), Me represents a divalent or trivalent metal atom, and Pc represents a phthalocyanine ring where hydrogen atoms on the ring may be replaced by halogen atoms.  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are identical or different and represent hydrogen atoms or  $\text{C}_{1-5}$  alkyl groups.  $\text{R}_4$  represents a hydrogen atom or a methyl group.  $n$  is 2 to 100, and  $(1 + m) = 1$  to 4.

[0030] Of these, the metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salts where, in aforesaid general formula (I), Me is Cu, Pc is a phthalocyanine ring in which the hydrogen atoms on the ring are not replaced by halogen atoms, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are identical or different and represent hydrogen atoms or C<sub>1-4</sub> alkyl groups, R<sub>4</sub> represents a C<sub>1-4</sub> alkyl {sic}<sup>i</sup> group, n is 20-50, and (1 + m) is 1 to 4, are particularly preferred.

[0031] Again, as a general formula for the optionally-halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salts favourably used in the present invention, besides the above, the metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salts represented by the following general formula (II) are preferred.

[0032]

[Chem. 6]



[0033] In general formula (II), Me represents a divalent or trivalent metal atom, and Pc represents a phthalocyanine ring where hydrogen atoms on the ring may be replaced by halogen atoms.  $R_1$ ,  $R_2$  and  $R_3$  are identical or different and represent hydrogen atoms or  $C_{1-5}$  alkyl groups.  $R_4$  represents a hydrogen atom or a methyl group.  $n$  is 1 to 100, and  $(1 + m) = 1$  to 4.

[0034] Of these, the metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salts where, in aforesaid general formula (II), Me is Cu, Pc is a phthalocyanine ring where the hydrogen atoms on the ring are not replaced by halogen atoms,  $R_1$ ,  $R_2$  and  $R_3$  are identical or different and represent hydrogen atoms or  $C_{1-4}$  alkyl groups,  $R_4$  represents a  $C_{1-4}$  alkyl group *(sic)*,  $n$  is 20-50, and  $1 + m$  is 1 to 4, are particularly preferred.

[0035] The component (B) used in the present invention, that is to say the unhalogenated metal phthalocyanine-sulphonic acid polyoxyalkyleneammonium salt or halogenated metal phthalocyaninesulphonic acid polyoxyalkyleneammonium salt can be obtained by generally-known methods.

[0036] For example, component (B) of the present invention can be produced in two stages as follows. In the first stage, aforesaid component (A) is heated and reacted with for example sulphuric acid, fuming sulphuric acid or chlorosulphonic acid, so that there is obtained an unhalogenated metal phthalocyaninesulphonic acid or a halogenated metal phthalocyaninesulphonic acid, or a metal salt thereof, after which in a second stage, using one 1 mol of this material plus 1-4 mol of an appropriate primary, secondary or tertiary amine type

organic acid salt or quaternary ammonium salt, heating and reaction are carried out in the normal way in water, organic solvent or mixed solvent with water. The materials with the respective aforesaid general formulae can of course be obtained in a similar way.

[0037] Thus, as the organic amine used at the time of the aforesaid heating and reaction, there can be employed an organic amine which contains polyoxyalkylene bonds. Specifically, there may be used polyoxypropyleneamine or other such primary amine, polyoxypropylenemethylamine, polyoxypropylene-ethylamine or other such secondary amine, polyoxydimethylamine {sic}<sup>ii</sup>, polyoxymethylethylamine {sic} or other such tertiary amine, or polyoxypropylenedimethylethylammonium chloride, polyoxytrimethylammonium {sic} chloride, polyoxypropylenemethyldiethylammonium chloride or other such quaternary ammonium salt.

[0038] The component (B) obtained in this way can be used directly, but it may also be used in any other form such as that of a wet cake or dry powder, following filtering, dewatering, drying, etc.

[0039] The pigment composition of the present invention contains both aforesaid component (A) and aforesaid component (B) as indispensable components, in proportions of 1 to 30 parts by weight and preferably 1 to 15 parts by weight of component (B) per 100 parts by weight of component (A).

[0040] The pigment composition can be readily obtained by thoroughly mixing together the aforesaid component



(A) and aforesaid component (B) by any known general method until uniform.

[0041] The mixing method at this time may comprise mixing in the powder state or adding as a wet cake, slurry or solution, or there can be employed a method whereby component (B), that is to say the optionally halogenated metal phthalocyaninesulphonic acid ammonium salt is formed by reaction in the presence of aforesaid component (A), that is to say the unhalogenated metal phthalocyanine or halogenated metal phthalocyanine pigment.

[0042] Furthermore, component (B) may be added in the stage for pulverizing coarse pigment comprising aforesaid component (A). When producing the ink, production does not only have to be carried out after mixing together (A) and (B) beforehand to form the composition, but the ink can also be produced by dispersing component (B) in an ink in which aforesaid component (A) has already been dispersed.

[0043] The gravure ink of the present invention can typically be obtained by mixing the pigment composition of the present invention as the colouring agent, plus solvent, with a liquid-form synthetic resin vehicle (C) and then ball-milling.

[0044] In the present invention, examples of the liquid synthetic resin vehicle (C) used in the preparation of the gravure ink include tall oil rosin, gum rosin, wood rosin, lime rosin, rosin ester, maleic acid resin, vinyl resin, polyamide resin, nitrocellulose, cellulose acetate, ethyl cellulose, ethylene-vinyl acetate

copolymer, urethane resin, polyester resin, alkyd resin, acrylic resin, gilsonite, dammar, shellac or other such resin, with these being employed on their own or in combination.

[0045] The gravure ink of the present invention can comprise for example 10-50 parts by weight of the liquid synthetic resin vehicle (C) and 30-80 parts by weight of one or more solvent such as a hydrocarbon, alcohol, ester, ketone, etherealcohol, ether, water or the like.

[0046]

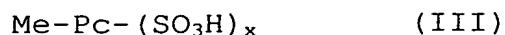
[Examples] Next, the present invention is explained by means of some examples and comparative examples. In these examples, all references to parts are on a weight basis.

[0047] Example 1

An acidic water-containing filter cake of the unhalogenated copper phthalocyaninesulphonic acid represented by the following formula (III) [the filter cake contained 3.5 parts of the copper phthalocyanine-sulphonic acid as pure component] and a water-containing filter cake of unhalogenated copper phthalocyanine [the filter cake contained 46.5 parts of the unhalogenated copper phthalocyanine as pure component] were dispersed in 3000 parts of water, and the pH adjusted to 8.0-8.5 with aqueous sodium hydroxide solution.

[0048]

[Chem. 7]

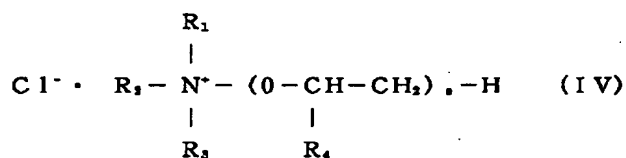


[0049] In formula (III), Me and Pc have the same meanings as above,  $x = 1-4$  and the average is 1.0.

[0050] Next, 8.41 parts of the polyoxypropylene ammonium chloride represented by formula (IV) below, in which the number of oxypropylene repeating units was 25 ( $n = 25$ ) [Adekacol CC36, produced by the Adeka Co.] was added and stirring carried out for 1 hour at 80-90°C, after which filtering was performed.

[0051]

[Chem.8]



[0052] In the formula (IV),  $\text{R}_1$  and  $\text{R}_2$  are  $\text{C}_2$  alkyl groups and  $\text{R}_3$  and  $\text{R}_4$  are methyl groups.

[0053] Next, washing was carried out with water until no more salt was present in the filtrate, following which drying was carried out at 90-100°C and, in this way, there was obtained 58.2 parts of a powder mixture of unhalogenated copper phthalocyanine and unhalogenated copper phthalocyaninesulphonic acid polyoxypropylene-ammonium salt (weight ratio of former/latter = 46.5/11.7).

[0054] The unhalogenated copper phthalocyanine-sulphonic acid polyoxypropyleneammonium salt obtained here is the compound where, in general formula (I) above,  $\text{Me} = \text{Cu}$ ,  $\text{R}_1$  and  $\text{R}_2$  are  $\text{C}_2$  alkyl groups,  $\text{R}_3$  and  $\text{R}_4$  are methyl groups,  $l = 0$ ,  $m = 1$  and  $n = 25$ .

[0055] 13 parts of isopropyl alcohol, 13 parts of ethanol, 7 parts of ethyl acetate and 30 parts of nitrocellulose resin varnish were added to 10 parts of this pigment composition and the mixture subjected to ball milling, to produce 73 parts of nitrocellulose-based gravure ink. Next, the fluidity and gloss were measured in the following manner. The measurement results are shown in Table 1.

[0056] Fluidity: Using a Brookfield viscometer (No.2 rotor or No.3 rotor), the viscosity of the gravure ink was measured under conditions of 20°C and 60 rpm. Gloss: The gravure ink was applied to a polyethylene film using a 0.15 mm bar coater, and then the gloss measured.

[0057] Example 2

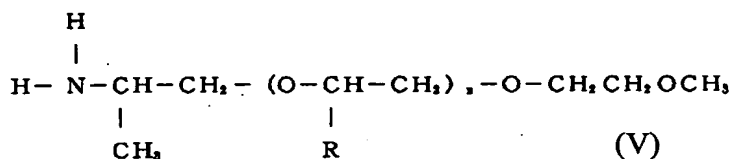
An acidic water-containing filter cake of unhalogenated copper phthalocyaninesulphonic acid identical to that in Example 1 [containing 3.5 parts of copper phthalocyaninesulphonic acid as pure component] and a water-containing filter cake of unhalogenated copper phthalocyanine [containing 46.5 parts of copper phthalocyanine as pure component] were dispersed in 3000 parts of water, and the pH adjusted to 8.0-8.5 with aqueous sodium hydroxide solution.

[0058] Next, 0.36 parts of 90% acetic acid was added to 10.69 parts of the polyoxypropyleneammonium (sic)<sup>iii</sup> of molecular weight 2,000 represented by the following formula (V) [Jeffamine M-2005, produced by the Huntsman Co.] and, after forming 11.05 parts of the

polyoxypropylene-ammonium acetic acid salt, stirring was carried out for 1 hour at 80-90°C and filtering performed.

[0059]

[Chem. 9]



[0060] In formula (V), R represents a hydrogen atom or methyl group, the ratio of these being 3/32. Furthermore  $n = 30.2$ .

[0061] Next, after washing with water until the filtrate no longer contained salt, drying was carried out at 90-100°C and there was obtained 60.6 parts of unhalogenated copper phthalocyanine and unhalogenated copper phthalocyaninesulphonic acid polyoxypropylene-ammonium salt (weight ratio of the former to the latter = 46.5/14.1).

[0062] The unhalogenated copper phthalocyanine-sulphonic acid polyoxypropyleneammonium salt obtained here is the compound where, in general formula (II) above,  $\text{Me} = \text{Cu}$ ,  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are hydrogen atoms,  $\text{R}_4$  is a hydrogen atom or methyl group where the molar ratio thereof is 3/32,  $l = 0$ ,  $m = 1$  and  $n = 30.2$ .

[0063] A nitrocellulose-based gravure ink was prepared in the same way as in Example 1 except that there was used the same amount of this pigment composition. Next, the fluidity and gloss were measured in the same way as

in Example 1. The measurement results are shown in Table 1.

[0064] Comparative Example 1

A nitrocellulose-based gravure ink was prepared in the same way as in Example 1 except that instead of the unhalogenated polyoxypropyleneammonium hydrochloride represented by aforesaid formula (IV), there was used 1.31 parts of dodecylammonium acetate. The fluidity and gloss were measured and the measurement results are shown in Table 1.

[0065] Comparative Example 2

A nitrocellulose-based gravure ink was prepared in the same way as in Example 1 except that instead of the unhalogenated polyoxypropyleneammonium hydrochloride represented by aforesaid formula (IV), there was used 1.45 parts of hexadecylammonium acetate. The fluidity and gloss were measured and the measurement results are shown in Table 1.

[0066]

[Tab.1]

Table 1

	Fluidity (cPa)	Gloss (60°)
Example 1	157	89.8
Example 2	112	98.1
Comparative Example 1	286	67.2
Comparative Example 2	723	84.9

[0067] As will be clear from Table 1, since the pigment composition of the present invention contains polyoxyalkylene bonds, excellent fluidity is shown compared to a conventional pigment composition containing material without such bonds. Furthermore, it is clear that a gravure ink containing this pigment composition can be employed for high speed printing, to give printed materials with a more outstanding gloss than hitherto.

[0068]

[Effects of the Invention] The pigment composition provided by the present invention has polyoxyalkylene bonds in the optionally-ring-halogenated metal phthalocyaninesulphonic acid alkylammonium salt molecules, so it is more outstanding in its fluidity and gloss and there is shown the outstanding effect of a markedly improved fluidity and gloss, which has not been possible with conventional pigment compositions containing an identical ammonium salt in which there are no polyoxyalkylene bonds.

### *Translator's notes*

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<sup>i</sup> Strictly speaking this would appear to be a broadening of the definition of  $R_4$ .

<sup>ii</sup> This would seem to be an error for polyoxypropylenedimethylamine.

<sup>iii</sup> Perhaps 'ammonium' here is an error for 'amine'.